

The Influence of Chemical Structure on the Dynamic Properties of Sulfur-Vulcanized, Carbon Black-Reinforced Natural Rubber

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Synopsis

A comparison is made of the composition and properties of the different rubber vulcanizate networks obtained by varying the ratio of sulfur to sulfenamide accelerator and by the thermal aging of vulcanizates containing predominantly polysulfide crosslinks. It is concluded that the changes in network structure which can take place, for example, during the service life of natural rubber tires are not the direct cause of failures of the type associated with rubber fatigue at high temperatures. However, a reduction in the total number of crosslinks can accelerate failure by increasing the amount of heat generated during flexing. More stable networks giving improved resistance to fatigue at high operating temperatures are obtained by the use of higher ratios of accelerator to sulfur than are conventionally employed.

INTRODUCTION

Cunneen and Russell^{1,2} have shown that in respect of natural rubber tires the development of the failure phenomenon known as tread looseness is accompanied by changes in the network structure of the tire rubber vulcanizate occurring under essentially anaerobic conditions.

The observed structural changes are characteristic of those which take place when polysulfide crosslinks mature under the action of heat. They include a reduction in the number of polysulfide linkages $R-S_x-R$, where R represents a polyisoprene chain and $x > 3$, an increase in the concentration of monosulfide linkages $R-S-R$ and an increase in the amount of sulfur bound to the network in the form of cyclic sulfide modifications of the polyisoprene chains. The initial crosslinks obtained with the concentrations of sulfur and N-cyclohexylbenzthiazole-2-sulfenamide (CBS) accelerator of the order conventionally employed with natural rubber and known to be employed in the tires concerned, e.g., 2.5 parts sulfur and 0.5 parts CBS per hundred parts of rubber, are predominantly polysulfidic.

The work to be described was undertaken to determine how far the changes in network structure reported by Cunneen and Russell are the direct

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cause of tread looseness and the other types of failure which appear to originate with the development of a crack or similar flaw within or beneath the tread region of tires.

FORMATION AND MATURATION OF SULFUR CROSSLINKS

The chemistry of the formation and maturation of sulfur crosslinks has been studied previously, particularly by workers at the laboratories of the Natural Rubber Producers' Research Association.³ It has been shown among other things that the polysulfide crosslinks initially formed during the accelerated sulfur vulcanization of natural rubber can undergo any of a number of competing reactions under the action of heat. One of the reactions involves the shortening of the polysulfide chains, a process catalyzed by accelerator complexes in the vulcanizate and able to occur repetitively until the crosslinks are reduced to monosulfides, with release of sulfur for further crosslinking. Alternatively, the initial polysulfide crosslinks may suffer elimination by thermal scission at the carbon-sulfur bond, leading to main chain modifications of the form of cyclic sulfides and changes in the olefinic structure of the polyisoprene molecules. A third reaction is interchange between polysulfide crosslinks at their points of attachment to the network chain. This can lead to stress relaxation but does not alter the crosslink composition of the network.

The competing reactions indicated above constitute the crosslink maturing process which controls the structure of the network during cure and seems likely to contribute to its behavior in service. The relative rates and extents of the various reactions are determined by a number of factors, not the least of which is the nature of the hydrocarbon group terminating the crosslink.⁴ The crosslink termini are, in turn, determined by the relative amounts of the sulfenamide accelerator and sulfur employed for vulcanization. When the accelerator:sulfur ratio is low, as in conventional vulcanization systems comprising, for example, 2.5 parts sulfur and 0.5 parts CBS phr and having an accelerator:sulfur weight ratio of 1:5, substitution by sulfur in the polyisoprene molecule occurs predominantly at carbon atoms α -methylenic to the double bond. The rate of desulfurization of dialkenyl polysulfides of this type is slow,⁵ and, in consequence, the crosslinks retain their predominantly polysulfidic form during vulcanization to be exposed to elimination and shortening when the vulcanizate is subjected to elevated temperatures while in service.

On the other hand, with efficient vulcanization (EV) systems having very high accelerator:sulfur ratios, of the order of 5:1 or more,⁶ substitution by sulfur in the polyisoprene molecules occurs chiefly at carbon atoms α -methylene to the double bond. The desulfuration of polysulfide crosslinks is very rapid in this instance, and there is little crosslink elimination or main chain modification. The maturing process is dominated by crosslink shortening and the formation of additional crosslinks with the liberated sulfur. A relatively stable network, containing predominantly monosulfide crosslinks, is

formed during vulcanization, and there is little scope for structural changes when the vulcanizate is subsequently subjected to heat.

Vulcanizates having predominantly monosulfide crosslinks are known to have different properties from those containing predominantly polysulfides. The former are considered to be inferior in respect of abrasion resistance, strength, and resilience and in flex cracking and cut growth resistance, depending on the conditions of test.⁷⁻⁹ Nevertheless, because monosulfide crosslinks impart superior aging resistance at temperatures of the order of 120°C or more,^{7,8} such as can be developed in tires, it seemed possible that the change from polysulfide to monosulfide crosslinks observed by Cunneen and Russell need not be entirely harmful.

EXPERIMENTAL

A study has been made of the effect of different sulfur crosslinks on some of the properties of a carbon black reinforced natural rubber vulcanizate considered to have a bearing on the type of rubber fatigue developed in tires at high temperatures. The different crosslink types were achieved, firstly, by subjecting vulcanizates prepared with a conventional combination of 3.0 parts sulfur and 0.6 parts CBS accelerator (phr) to thermal aging under vacuum and, secondly, by varying the amounts of sulfur and CBS in the rubber compound so as to alter the crosslink type without changing the type of accelerator. Studies of the effect of crosslink type and concentration on certain vulcanizate properties have previously been carried out by Studebaker.¹⁴

Among the vulcanizate properties determined were tear resistance over a range of extension rates and temperatures and the elastic and viscoelastic (loss) components of the dynamic compression modulus, Y' and Y'' , respectively. According to Collins, Jackson, and Oubridge,¹⁰ the total energy losses in tires can be considered as the sum of those occurring under constant stress amplitude conditions, which are proportional to $Y''/(Y')^2$, and those occurring under constant strain amplitude conditions, which are proportional to Y'' .

Also determined was the performance of vulcanizates in the Dunlop Punch Test in which cylindrical specimens, 3 in. high and 2 in. in diameter, are subjected to cyclic compressions at a constant rate under conditions of constant energy input.¹¹ Compared to the situation with tires, energy losses in the punch test relate inversely to resilience and are directly proportional to Y''/Y' . Arising particularly from its effect on the elastic modulus, Y' , vulcanizate crosslink density has a marked influence on energy losses in the Dunlop Punch Test and in tires under constant strain amplitude conditions.¹³

The significance of the punch test in the context of the present work is that it is a form of high-temperature fatigue test which seems to reproduce the mode of tread looseness failure in tires. The failure of punch test pieces terminates with a surface "blowout" which is the result of the growth of a

small flaw initiated within the vulcanizate under anaerobic conditions.^{12,13,15} Moreover, it will be apparent that, in the course of punching, conventional vulcanizates undergo the characteristic change from poly- to monosulfide crosslinks observed in tires.

Preparation of Vulcanizates

Compounding was carried out using a two-stage mixing process involving the addition of accelerator and sulfur to portions of a masterbatch on a mill at 60–70°C. The masterbatch, comprising rubber, carbon black, and the other compounding ingredients, was prepared in a 00 Banbury mixer. The compounds were designated conventional, increased accelerator (IA), or very high accelerator (VHA), according to the ratio of CBS to sulfur in the completed mix (Table I).

TABLE I
Compound Formulae

Masterbatch*			
Natural rubber			100.0
Stearic acid			1.0
Zinc oxide			7.5
Pine tar			7.0
Antioxidant			1.5
HMF black			35.0
			152.0
Compounds*	Conventional	IA	VHA
Masterbatch	152.0	152.0	152.0
CBS	0.6	2.2	9.0
Sulfur	3.0	1.4	0.6

* Parts by weight

The concentrations of sulfur and CBS accelerator chosen for the IA and VHA compounds were those which a preliminary experiment indicated would give similar values for Y' at 30°C for vulcanizates cured for 50 min at 135°C. These conditions of vulcanization are found to give near-maximum crosslinking with the conventional compound.

In addition to the vulcanizate cured for 50 min, a group of vulcanizates from each compound was cured for 80 min at 135°C in order to ascertain the effect of a relatively short period of heat aging such as might occur during a severe overcure. The test-pieces for the Dunlop Punch Test were molded in duplicate to allow the composition of the networks to be determined before and after flexing.

Physical Testing of Vulcanizates

The Dunlop Punch Test was carried out using the machine and procedure described in detail elsewhere.^{11,13} The performance of vulcanizates in the

test was measured as the time to failure in minutes and as the punch performance rating. The latter is the logarithm of the number of deflections to failure and is a convenient way of expressing a measure of the logarithm of the life. A difference in punch performance rating of the order of 0.25 is required for significance between two determinations.

The punch performance rating of comparable vulcanizates is inversely proportional to the energy loss (Y''/Y') which can be measured as the running temperature generated in the test-piece in the course of punching.^{11,13} Only differences in punch performance rating at comparable running temperatures are considered to indicate differences in fatigue resistance. Differences in running temperature of the order of 15°C or more are required for significance between two determinations.

A rotary power loss machine¹⁶ was used to determine the elastic and loss components of the dynamic modulus over a range of temperatures.

Tear testing was carried out on "crescent" test-pieces (ASTM D 624) over a range of extension rates and temperatures, using machines performing similar functions to those respectively described by Kainradl and Händler¹⁷ and Gurney, Jones, and Beeson.¹⁸

Determination of Structure Characteristics of Punch Test-Pieces

Concentric cylindrical plugs were removed along the vertical axis of the test-piece by means of a lubricated cork borer attached to a power drill. The plugs were cut into discs, approximately 1 mm thick, by a technique similar to that described for the treatment of plugs taken from tires.¹

Information concerning the composition of the sulfur crosslinks in the discs was obtained by analyses involving chemical probe techniques. The methods have been reviewed by Saville and Watson¹⁹ and are similar to those used in the tire studies.^{1,2}

The values of E , the number of sulfur atoms combined in the vulcanizate network per chemical crosslink present, and E' , the number combined after treatment with triphenylphosphine, were also determined. The quantity E gives information on the structural complexity of the network, while $E' - 1$ is the number of sulfur atoms combined in the network in the form of main chain modifications per crosslink,^{4,19} assuming no carbon-carbon crosslinks are present.

Thermal Aging Under Vacuum

Vulcanized punch test-pieces of the conventional compound (3.0 sulfur/0.6 CBS) were sealed in a glass ampoule under vacuum for immersion in an oil bath for 1000, 1800, 4000 and 8000 min at 143°C. The punch life of the corresponding unaged vulcanizate is of the order of 1000 min at this temperature. The periods of aging under vacuum were extended well beyond this time to ensure that the required changes in network structure would take place. It was argued that if failure in punch test-pieces (and in tires) was due to the changes in network structure which include the change to

monosulfide linkages, at least those test-pieces subjected to the longer periods of thermal aging should fail very quickly.

CROSSLINK CHANGES INDUCED BY THERMAL AGING

Figure 1 illustrates the composition of the crosslinks at the center of punch test pieces made from the conventional compound (Table I) before and after thermal aging under vacuum and again after the aged and unaged vulcanizates have been flexed to failure in the Dunlop punch machine. Some of the information in Figure 1 is included in Table II for comparison with the physical properties of the vulcanizates.

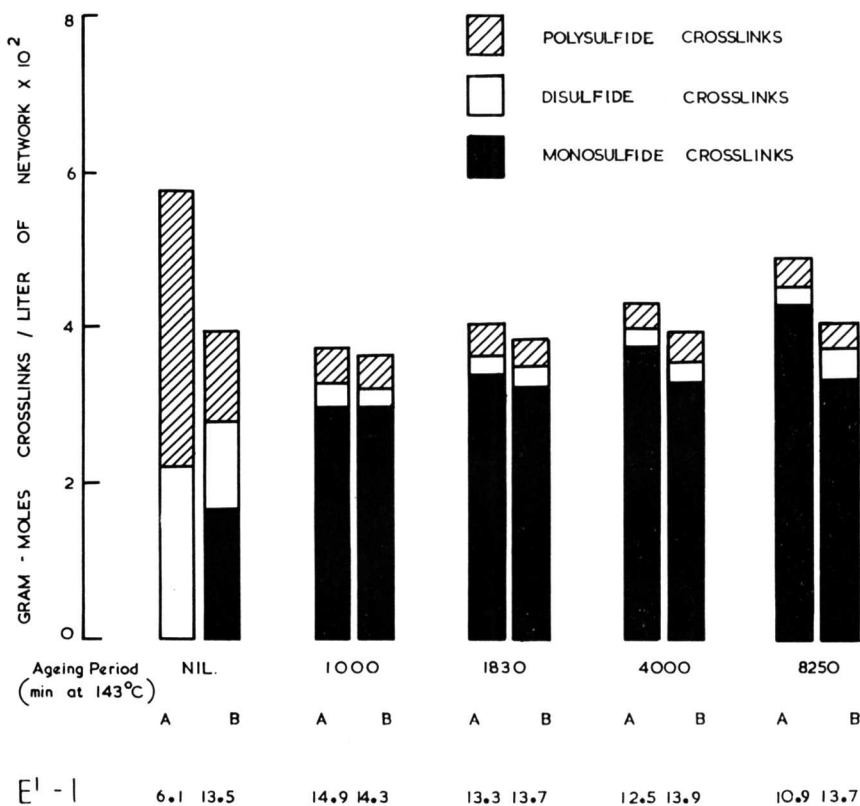


Fig. 1. Network composition of unaged and aged vulcanizates of the conventional compound (3.0 phr sulfur, 0.6 phr CBS) before (A) and after (B) punch testing.

It is apparent from Figure 1 that considerable structural changes take place during the punching of the unaged vulcanizate of the conventional compound. As was found in the case of tires,¹ a reduction in the number of crosslinks present as di- and polysulfides is accompanied by the appearance of monosulfide crosslinks, which constitute a significant proportion of the total by the time failure occurs. Nevertheless, the change to monosulfide

TABLE II
Vulcanizates Heat Aged in Vacuum^a

	Nil	Aging period, mins at 143°C			
		1000	1830	4000	8250
g-Moles crosslink/liter network $\times 10^2$	5.73	3.64	4.01	4.29	4.87
E	13.3	17.9	15.1	14.4	12.7
$E' - 1$	6.4	14.9	13.3	12.5	10.9
Dunlop Punch Test					
Performance rating ^b	5.26	5.02	5.35	5.16	5.21
Life, min	975	556	1200	770	874
Running temperature, °C	142	175	168	170	170
Rotary Power Loss Test					
Resilience, %, at:					
	89	83	84	83	83
	91	85	86	87	86
	93	86	89	89	89
	92	86	89	90	91
Elastic Modulus (Y'), kg/cm ² at:					
	53	44	44	50	
	50°C	51	42	46	
	80°C	50	41	45	
	110°C	39	40	44	
Loss modulus (Y''), kg/cm ² at:					
	2.0	2.6	2.5	2.9	
	1.5	2.2	2.1	2.1	
	1.0	1.9	1.6	1.7	
	1.3	1.9	1.5	1.5	
	1.50	2.15	1.92	2.05	
average	0.7	1.3	1.3	1.2	
$Y''/(Y')^2 \times 10^3$ at:					
	30°C	0.6	1.1	1.0	
	50°C	0.5	0.9	0.9	
	80°C	0.5	0.9	0.9	
	110°C	0.5	0.9	0.8	

^a Compound: Conventional in Table I (3.0 phr sulfur, 0.6 phr CBS); cure: 50 min at 135°C

^b Log number of deflections to failure.

linkages has proceeded to a lesser extent in the course of punching than that developed at the shortest period of maturing under vacuum.

It has already been shown^{2,4} that vulcanizates of conventional-type compounds lose crosslinks when aged at about 140°C in the absence of air. Figure 1 indicates that the total number of sulfur crosslinks is also reduced in the course of punching, which can be regarded as a form of thermal aging under dynamic conditions. Moreover, whether due to punching or aging under static conditions for a similar time at a similar temperature, the loss of crosslinks is associated with an increase in the amount of sulfur attached to the polyisoprene chain in the form of cyclic sulfides as defined by $E' - 1$. The changes in crosslink density and crosslink type occurring during punching appear analogous to those previously reported by Studebaker¹⁴ in respect of the Goodrich flexometer.

Figure 1 suggests that, if the period of thermal aging is prolonged beyond the punch life of the unaged vulcanizate, the total number of crosslinks increases with time of aging while, as is to be expected, the value of $E' - 1$ diminishes. Whether this is indicative of crosslinks being reformed from cyclic sulfides on prolonged aging or of the inclusion of carbon-carbon crosslinks in an otherwise stable sulfur network is uncertain.

The performance rating of conventional-type vulcanizates in the Dunlop Punch Test has been shown to relate inversely to the temperature generated in the course of punching¹¹ and directly to resilience at punch operating temperatures.^{13,23} It is influenced by state of cure, by virtue of the latter's effect on resilience, and more especially on the elastic and loss moduli²² (resilience $\approx 1 - \pi Y''/Y'$). For these reasons the tendency shown in Table II, particularly at high temperatures, for the elastic modulus and the resilience of the aged and unaged vulcanizates to vary with crosslink density is in accord with the norm, although Bristow and Tiller²¹ have shown that, at 21°C, resilience also depends on network structure. Some indication of a relationship between resilience and the temperature generated on punching is also to be expected.

The unusual feature of the information contained in Table II is that, with reference to the punch performance rating and running temperature of the unaged vulcanizate, the punch performance ratings of the aged vulcanizates are appreciably better than could be anticipated from their running temperatures. This apparently reflects the superior heat fatigue resistance of the networks formed by thermal aging.^{7,8} Only in the case of the vulcanizate aged for 1000 min at 143°C is a fall in crosslink density sufficient to give a significant reduction in punch performance rating relative to that of the unaged vulcanizate.

As to the loss modulus, which can be considered to contribute to energy losses under both constant stress amplitude and constant strain amplitude conditions, while the average values for Y'' obtained over the range of test temperatures may relate directly to $E' - 1$ (Table II), the differences in the values of the first-mentioned parameter are small and of the order to be expected from the changes in crosslink density. Indeed, the punch per-

formance rating apart, all the changes in the high-temperature dynamic properties, obtained by thermal aging and shown in Table II, can be ascribed to differences in crosslink density. However, as the reductions in crosslink density appear to be small in the machine and road tested tires studied by Cunneen and Russell,¹ it seems unlikely that effects associated with changes in crosslink density could have made a significant contribution to their failure.

It is of interest that Gough and Parkinson noted in their original work¹¹ that vulcanizates have remarkably good punch lives after oven aging in which, presumably, at least surface oxidation takes place quite apart from any crosslink changes of the type induced in this study.

EFFECTS OF SULFUR:ACCELERATOR RATIO

The sulfur crosslinks obtained with the conventional, increased accelerator (IA), and very high accelerator (VHA) compounds on vulcanization at 135°C appear from Table III to conform with the expected pattern.^{4,6} After 50 min, the conventional vulcanizate contains mainly polysulfide crosslinks, the VHA predominantly monosulfide, and the IA mainly di- and polysulfide types with an appreciable number of monosulfide linkages in addition. In all three cases, extending the cure time to 80 min is found to increase the numbers of di- or monosulfide crosslinks at the expense of the higher-ranking types. Changes in crosslink density, confirmed apparently by changes in elastic modulus, Y' (Table III), show that the conventional vulcanizate loses sulfur crosslinks if the cure is extended from 50 to 80 min, whereas the IA and VHA vulcanizates are little affected in this respect.

A plot of crosslink density against elastic modulus, Y' , at 30° and 120°C for the conventional, IA, and VHA vulcanizates is shown in Figure 2 in relation to the graph of the corresponding data for the vulcanizates given in Table II. The results for the VHA vulcanizates are seen to conform with an apparently general crosslink density-elastic modulus relationship at 120°C but not at 30°C. At the lower of the two temperatures, the VHA vulcanizates have higher elastic modulus than could be anticipated from crosslink density determinations. They appear at low temperatures to have a greater network structure than the numbers of sulfur crosslinks can account for.

The Y' values for the VHA vulcanizates decrease more rapidly than those of the others as the temperature is raised, but are not appreciably less than those of some of the others at 110°C (Table III). This suggests that the cause of the relatively high loss component (Y'') of the hysteresis (Y''/Y') is the major factor contributing to the low resilience of the VHA vulcanizates at high temperatures and their associated high running temperature and poor performance in the Dunlop Punch Test.

The punch performance ratings of the IA vulcanizates (1.4 phr sulfur, 2.2 phr CBS) are superior to those of the conventional (3.0 phr sulfur, 0.6 phr CBS), although the resilience of these vulcanizates and their temperature

TABLE III
 Crosslink Modification by Curative Adjustment. Structural Features and Dynamic Properties of Vulcanizates
 Cured for 50 and 80 Minutes at 135°C

	Conventional compound		Increased accelerator (IA) compound		Very high accelerator (VHA) compound	
	50 min	80 min	50 min	80 min	50 min	80 min
g-Moles crosslink/liter network $\times 10^2$	4.35	3.71	4.34	4.28	4.13	3.97
Polysulfide crosslinks, %	64	54	46	33	19	18
Disulfide crosslinks, %	36	46	37	49	18	12
Monosulfide crosslinks, %	0	0	17	18	63	68
Dunlop Punch Test						
Performance rating ^a	5.13	4.99	5.32	5.38	4.48	4.42
Life, min	770	540	1200	1350	175	150
Running temperature, °C	147	155	143	155	>200	>200
Rotary Power Loss Test						
Resilience, %, at:						
	87	87	87	87	82	83
	90	88	89	87	80	83
	91	91	90	90	84	82
	91	91	90	90	83	84
Elastic modulus (Y'), kg/cm ² , at:	50	42	50	47	54	55
	49	41	49	45	49	51
	48	39	48	45	41	45
	47	37	48	43	40	42
Loss Modulus (Y''), kg/cm ² , at:	2.2	1.9	2.2	2.0	3.3	3.3
	1.6	1.6	1.8	1.6	3.4	3.1
	1.4	1.1	1.5	1.5	2.3	2.8
	1.4	1.1	1.6	1.5	2.3	2.3
$Y''/(Y')^2 \times 10^3$, at:	0.9	1.1	0.9	0.9	1.1	1.1
	0.7	1.0	0.8	0.8	1.4	1.2
	0.6	0.7	0.7	0.7	1.4	1.4
	0.6	0.8	0.7	0.8	1.4	1.3

^a Log number of deflections to failure.

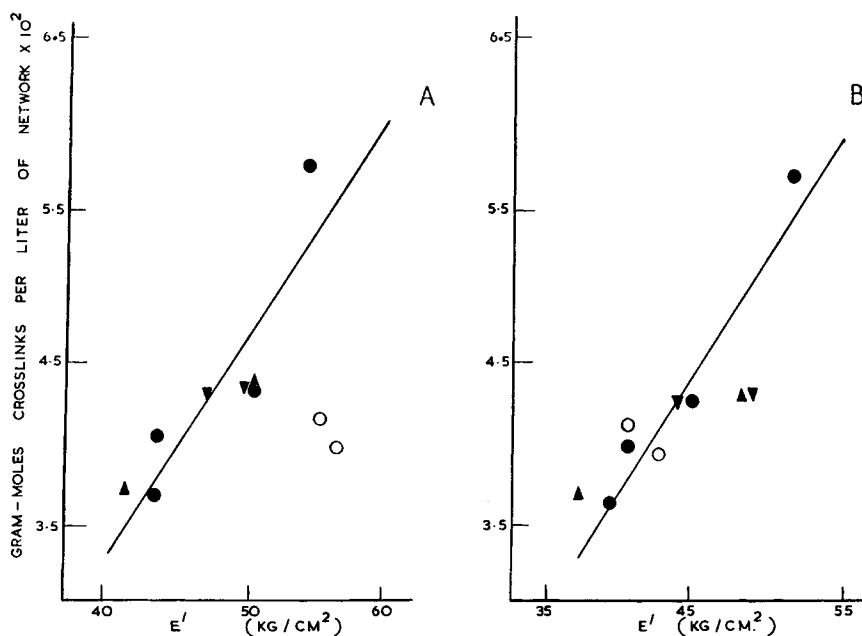


Fig. 2. Plot of crosslink density against elastic modulus for the conventional (▲), IA (▼), and VHA (○) compounds in Table III in relation to corresponding graph for the aged and unaged vulcanizates in Table II (—●—) at 30°C (A) and 110°C (B).

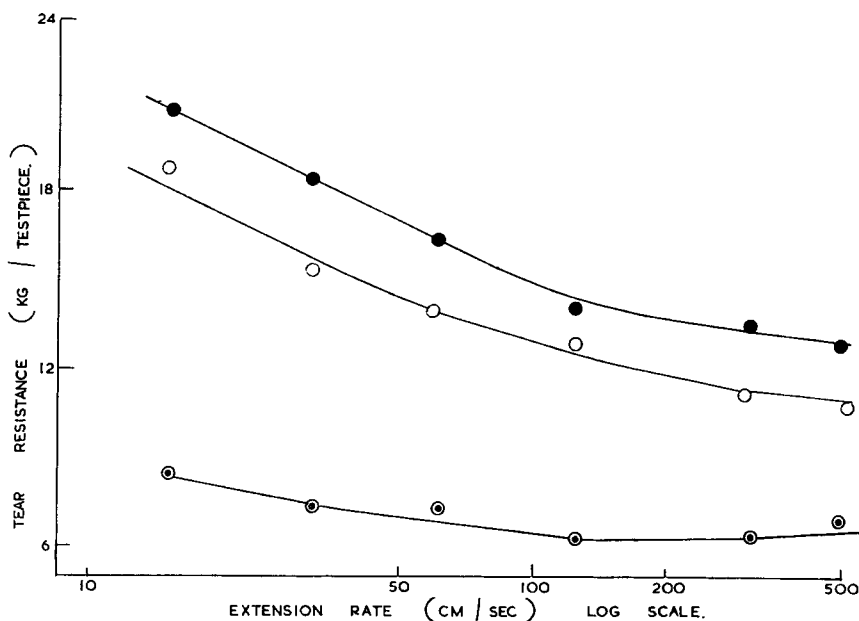


Fig. 3. Effect of extension rate on the tear resistance at 21°C of vulcanizates of the conventional compound (●), the IA compound (○), and the VHA compound (⊙).

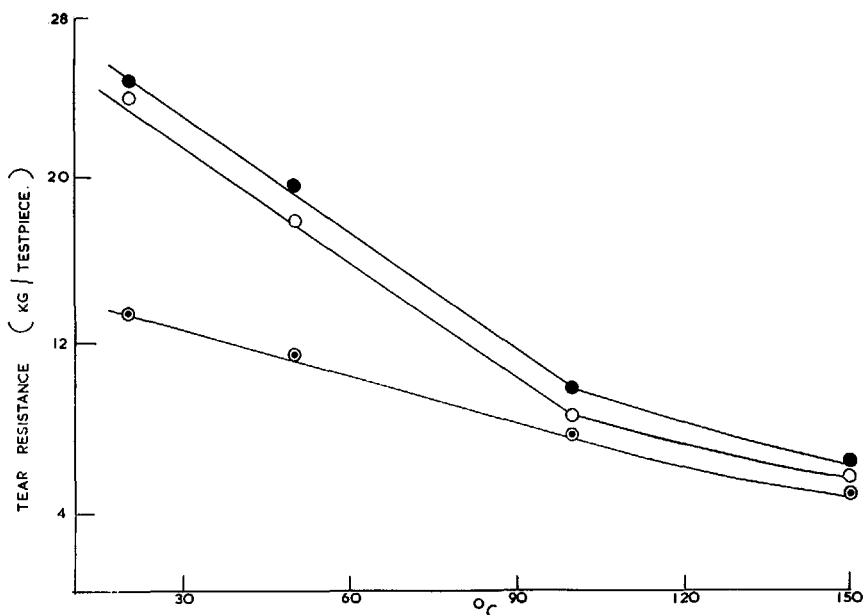


Fig. 4. Effect of temperature on the tear resistance of the conventional compound (●), the IA compound (○), and the VHA compound (⊙) at an extension rate of 0.85 cm/sec.

generation in the Dunlop Punch Test are not significantly different (Table III). The indication that the punch performance of the conventional compound undergoes a downward trend on increasing the cure time from 50 to 80 min, in accord with the effects of cure time on the elastic modulus, is within the limits of experimental error. In general, however, the findings outlined above are consistent with the view that short sulfur crosslinks can give improved high-temperature fatigue resistance, other things being equal, because of their greater heat stability.^{7,8,20} Another factor appears to be introduced in the case of the VHA vulcanizates studied, which promotes high running temperatures and counters any advantage in heat stability which should be forthcoming from the high concentration of monosulfide linkages.

Gough and Parkins¹¹ suggest that tear phenomena may play a part in the development of failure in punch test-pieces. In this connection, Figures 3 and 4 show, respectively, that differences in tear resistance due to crosslink type are largely maintained over a wide range of extension rates (which include those considered applicable to tires) but diminish as the temperature approaches that generated during punching.

DISCUSSION

The attainment of parity in the number of sulfur crosslinks in vulcanizates of the conventional, IA, and VHA compounds requires a very high

loading of CBS in the last-mentioned stock, so much so that the accelerator becomes one of the major constituents of the compound (Table I). Campbell²⁴ has shown that vulcanizates prepared from compounds having the same ratio of accelerator to sulfur as the VHA compound, but having somewhat lower sulfur and accelerator concentrations, contain main chain modifications comprising pendant accelerator fragments in amounts of the order of 67% of the molar concentration of sulfur crosslinks.

The relatively high temperature dependence of the elastic modulus of the VHA vulcanizates is in accord with Campbell's²⁴ view that pendant groups can provide a certain amount of secondary interaction between polymer chains which is weaker than covalent crosslinks and labile at elevated temperatures. Using the information in Figure 2, one can calculate a concentration of pendant groups in the VHA vulcanizates of the order of 75% of the concentration of sulfur crosslinks at 30°C, assuming one secondary interaction involves two pendant groups. Whether such pendant groups are the cause of the high loss modulus and inferior punch performance of the VHA vulcanizate is not apparent. Clearly, however, a correspondingly high concentration of accelerator pendant fragments is not formed in vulcanizates of the conventional compound when a change from polysulfide to monosulfide crosslinks is induced by thermal aging.

Just as increasing the accelerator:sulfur ratio does not reproduce the network structures which develop when vulcanizates are thermally aged,⁹ so neither does aging under static conditions reproduce all the changes of a morphologic nature which occur when vulcanizates mature under dynamic conditions. If the static and dynamic aging processes are identical, the vulcanizates matured under vacuum at high temperature (Table II) should fail soon after being subjected to punching. The good punch performance of the heat-matured vulcanizates of the conventional compound supports the view of Gough and Parkinson¹¹ that mechanical work plays an essential part in high-temperature rubber fatigue quite apart from its effect on temperature. Failure is not simply due to heat, although it makes an important contribution.

It has been proposed that, as is considered to be the case with metals, flexing initiates a flaw which develops according to laws that control such a phenomenon.¹⁵ The tendency for differences in their tear resistance to diminish as the temperature is raised (Fig. 4) indicates that flaw propagation may proceed at a similar rate in the vulcanizates studied, under punch testing conditions. Be this as it may, data obtained by Gough and Parkinson¹¹ gives an activation energy of 17 kcal/mole for the failure process, suggesting that essentially chemical mechanisms determine the magnitude of differences in the overall failure rate.

CONCLUSIONS

The changes in network structure associated with the maturing of the polysulfide linkages initially formed in tires cured with the conventional

sulfur-sulfenamide accelerator systems are not the direct cause of tread looseness or other failures having their origin in rubber fatigue at high temperatures. However, when the changes include a reduction in the number of crosslinks, the latter may accelerate the failure process by increasing the amount of heat generated within the tire.

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